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POLYOLS CONTAINING CARBOXYL GROUPS  
AND PRODUCTION THEREOF

CROSS-REFERENCE TO RELATED APPLICATIONS

10 This application is a Continuation-in-Part application of U.S. Patent Application No.  
09/723,263 filed November 27, 2000.

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates generally to low viscosity polyols suitable for use in the synthesis of polyurethanes, and, more particularly, to carboxyl-containing polyols. These carboxyl-containing polyols are made by reacting a low molecular weight polyol with a dicarboxylic acid anhydride in the presence of 5-500 ppm of a catalyst selected from the group consisting of organic acids, inorganic acids, and combinations thereof.

2. Description of the Related Art

It is well known that polyurethanes are generally manufactured by reacting a polyisocyanate and a polyol. The resulting polyurethane may have unique chemical and/or mechanical properties depending on the reacting conditions, as well as other additives such as catalysts, solvents, surfactants, blowing agents, fillers, and the like. The polyols used in manufacturing polyurethanes are typically low molecular weight poly-hydroxyl-containing polymers, such as those containing polyethers, polyesters, polyacrylics, polycarbonates, and the like. These polyols are generally provided with at least two hydroxyl groups so that they can be easily incorporated into a lengthening polymer in an ordered fashion.

Due to environmental and toxicity concerns, water-based polyurethanes and aqueous dispersions of polyurethanes are becoming the preferred materials for many applications, including coating applications. However, in many instances, the components of the polyurethane

including coating applications. However, in many instances, the components of the polyurethane product are not easily soluble in water. To overcome this problem, it is known to introduce ionizable groups into the monomers prior to their condensation into the final polyurethane polymer. These ionizable groups aid in the solubilization of the polymer and thus produce a uniform aqueous dispersion of the final polyurethane mixture.

The reaction of dicarboxylic acid anhydride with triols or tetrols has been described generally in U.S. Patent No. 5,863,980 to Kuen-Bae Choi. According to the disclosure, acid groups are attached to the main chain via an ester bond in the absence of catalysts, including acid catalysts. In order to perform the reaction between acid anhydride and polyol, a high reaction temperature was used and resulted in highly viscous polyols. When such highly viscous polyol is reacted with a diisocyanate, a viscous prepolymer is obtained, and this result is not desired since the viscous prepolymer is difficult to process.

U.S. Patent No. 4,207,2267 to Wulf von Bovin discloses a process for preparation of stable suspensions of inorganic fillers in poly-hydroxyl compounds by grafting olefinically unsaturated carboxylic acid onto polyol. As an example, acrylic acid and peroxide type initiators are used for this process.

U.S. Patent No. 4,250,077 to Wulf von Bovin et al. discloses a suspension which is stable and contains inorganic filler and graft polymer which was produced by free radical polymerization of olefinically unsaturated carboxylic acid.

U.S. Patent No. 4,460,738 to Frentzel et al. discloses a process for grafting carboxyl groups to mono and polyether polyols by reacting maleic acid, fumaric acid, itaconic acid or their mixtures with polyether polyols in presence of peroxy-type free radical initiator.

U.S. Patent No. 4,521,615 to Frentzel discloses carboxy-containing polyols made by a free radical type addition reaction of fumaric or maleic acid with a monoether or a polyether diol or triol. It is stated at column 6, lines 37-44 of the Frentzel patent that some or all of the carboxylic acid groups on the carboxy-containing polyols can be neutralized with an organic or inorganic base. This patent also discloses that the polyols are suitably further reacted to form prepolymers, and the carboxyl groups on the prepolymer are suitably neutralized, e.g. with triethylamine (TEA), for forming dispersions (see column 7, lines 42-60).

U.S. Patent No. 6,103,822 to Housel et al. discloses a process for incorporating carboxyl groups into main polyester chain by reacting polyether or polyester polyol with an aliphatic dianhydride.

U.S. Patent Nos. 5,242,954 and 5,250,582 to Hire et al. disclose a process for making cellular and microcellular polyurethane foams using a carboxylic acid-grafted polyol.

U.S. Patent No. 5,880,250, discloses the reaction of polyols with dianhydride "to form an acid functionalized polyol in which there are reactive hydroxyl groups, and neutralizable or reactive carboxylic acid groups." See Formula II at column 7 of the '250 patent. There are three ways by which carboxyl groups can be introduced into the polyol component:

1. Free Radical addition of unsaturated dicarboxylic acids to polyol through C-C double bond (U.S. Patent Nos. 4,207,2267; 4,250,077; 4,460,738; 4,521,6155; 242,954 and 5,250,582)
2. Reacting a polyol with a dianhydride and producing polyester type bonding ( U.S. Patent Nos. 6103822; 5,880,250)
3. Reacting a triol or tetrol with an anhydride of dicarboxylic acid which binds the carboxyl group to polyol through an ester bond (U.S. Patent No. 5,863,980)

A common result of introduction of a carboxyl group into the polyol component, in accordance with the U.S. Patent No. 5,863,980 is that undesirable side reactions occur between the carboxyl group and nearby hydroxyl groups. The side reactions, typically causing oligomers to form, markedly increase the viscosity of the monomer mixture, resulting in a decreased amount of usable monomers suitable for use in the final aqueous urethane dispersion. In addition, the "side" reacted carboxyl group results in reduced hydrophilicity of the final urethane dispersion.

Accordingly, there is a need for low viscosity polyols containing carboxyl groups, and methodology for their production. Further, there is a need for low viscosity polyols that are suitably water soluble, and are useful in the preparation of low viscosity urethane dispersions. The present invention provides an answer to those needs.

#### SUMMARY OF THE INVENTION

In one aspect, the present invention is directed to a low viscosity carboxyl-containing polyol composition having a viscosity in the range of 3,000 – 100,000 centipoise, and having an

oligomer content of less than 30 g KOH/gm. This composition is obtained by reacting a polyol containing between two and four hydroxyl groups with an anhydride of a dicarboxylic acid. Preferably, the polyol reactant is a triol, and the carboxyl-containing polyol has one ester group and one carboxyl group per molecule. The carboxyl-containing polyol is suitable for use in preparing low viscosity polyurethane prepolymers.

In another aspect, the present invention is directed to a method of producing this carboxyl-containing polyol composition by reacting a low molecular weight polyol containing between two and four hydroxyl groups and preferably a triol with a dicarboxylic acid anhydride in the presence of 5-500 ppm of an inorganic or organic acid catalyst, forming an ester bond containing the carboxyl group. The organic or inorganic acid is preferably selected from the group consisting of hydrochloric acid, sulfuric acid, nitric acid, formic acid, propionic acid, p-toluenesulfonic acid, oxalic acid, and combinations thereof.

In yet another aspect, the present invention is directed to a method of preparing a carboxyl-containing monomer for use in preparation of a polyurethane polymer, comprising the step of combining a low molecular weight polyol compound and an dicarboxylic acid anhydride in the presence of 5-500 ppm of an organic or inorganic acid (advantageously selected from the group consisting of hydrochloric acid, sulfuric acid, nitric acid, formic acid, propionic acid, p-toluenesulfonic acid, oxalic acid, and combinations thereof, in order to produce the carboxyl-containing monomer, the carboxyl-containing monomer having a viscosity in the range of about 3,000 to about 100,000 cps and having an oligomer content of less than about 30 mg KOH/g.

In still another aspect, the present invention relates to a prepolymer that is formed by reacting the carboxyl-containing polyol, or a partially or fully neutralized amine salt thereof, with a polyisocyanate.

In another aspect, the present invention is directed to a water-borne polyurethane polymer, the water-borne polyurethane polymer being the reaction product of (1) the prepolymer described above, and (2) an amine compound.

These and other aspects will become apparent upon reading the following detailed description of the invention.

## DETAILED DESCRIPTION OF THE INVENTION

It has been surprisingly found, in accordance with the present invention, that a low viscosity carboxyl-containing polyol composition having a viscosity in the range of about 3,000-100,000 centipoise, and having an oligomer content of less than 30 mg KOH/g, is suitably prepared in a straightforward fashion. Preferably, the carboxyl-containing polyol has one ester group per molecule. The carboxyl-containing polyol is suitable for use in preparing low viscosity polyurethane prepolymers.

Further, the present inventors have surprisingly discovered that the reaction of a low molecular weight polyol with an dicarboxylic acid anhydride, suitably effected in the presence of an organic or inorganic acid catalyst, suitably provides a low viscosity carboxyl-containing polyol that can be advantageously employed in the production of low viscosity polyurethane prepolymers for waterborne polyurethane dispersions. Also, the present inventors have unexpectedly discovered that organic and inorganic acid catalysts are very efficient in catalyzing polyol-anhydride addition reactions with anhydride ring opening mechanism, while exhibiting little or no acceleration of acid and polyol condensation side reactions.

The present invention provides a process for introducing carboxyl groups to polyol monomers, and the low-viscosity carboxyl-containing polyol monomers made by the process. The carboxyl-containing polyols are prepared by reacting a polyol monomer, preferably containing three hydroxyl groups per molecule, with a dicarboxylic acid anhydride under conditions such that an organic acid group is introduced into the polyol monomer. Because the polyol monomer is preferably selected to have three hydroxyl groups per molecule and is reacted with only one molecule of anhydride, the resulting carboxyl-containing monomer possesses two free hydroxyl groups per molecule and one carboxyl group attached to the polyol. As indicated above, the two free hydroxyl groups of the carboxyl-containing monomer are used in subsequent reactions that form the ultimate polyurethane, while the carboxyl group aids in hydration of the polyurethane dispersion and prevents generation of highly viscous, unwanted side reactions and undesirable by-products.

As defined herein, the term "polyol" refers to compounds having between two and four free hydroxyl (-OH) groups per molecule, and preferably three hydroxyl groups. As defined herein, the phrase "low molecular weight polyol" refers to those polyols having a molecular weight less than 8,000, more preferably less than 2,000, and most preferably less than 500. The

phrase "carboxyl-containing monomer" refers to a polyol having a carboxyl group added to one of the hydroxyl groups of the polyol. The term "oligomer" refers to a product where more than one polyol molecule is reacted with an acid anhydride.

As indicated above, in one aspect, the present invention is directed to a carboxyl-containing polyol that is suitable for use in preparing a polyurethane polymer. The carboxyl-containing polyol is the reaction product of a low molecular weight polyol compound and a dicarboxylic acid anhydride, and the resulting carboxyl-containing monomer has a viscosity in the range of 3,000-100,000 centipoise (cps) and has oligomer content in the range of 2-30 mg KOH/g. Each of these components are discussed in more detail below.

Examples of polyols that are useful in the present invention include low molecular weight polyols having from two to four hydroxyl groups. Preferably, the polyol contains three free hydroxyl groups (hereinafter termed "triol"). Triols suitable for use in the present invention are generally based on the structure of glycerol, trimethylolpropane, trimethylolethane, triethanolamine, triisopropanolamine and the like. Preferred triols include Poly-G 76-635 (a polyether triol of nominal molecular weight 265, available from Arch Chemicals, Inc.) and Poly-G 35-610 (a polyether triol of nominal molecular weight 275), and their mixtures with trimethylolpropane or pure trimethylolpropane. Alternatively, polyalkylene polyether polyols produced by the poly-addition of any of the mentioned above triols and an alkylene oxide such as ethylene oxide, propylene oxide, butylene oxide, epoxybutene, and the like, may also be used. These triols generally have molecular weight from less than 100 to about 6000.

Suitable acid anhydrides used in the present invention include any dicarboxylic acid anhydride that results in the addition of a carboxyl group to the polyol molecule. Useful acid anhydrides include maleic anhydride, phthalic anhydride, succinic anhydride, glutaric anhydride, and mixtures thereof. A preferred acid anhydride is succinic anhydride.

The preparation of the carboxyl-containing polyol is generally accomplished by reacting the low molecular weight triol compound with a dicarboxylic acid anhydride in the presence of an inorganic or an organic acid catalyst. Advantageously, the resulting product has one ester bond per molecule. When employing an inorganic acid catalyst, the polyol is suitably heated with anhydride to about 80-105°C in presence of the inorganic acid (preferably about 25-500 ppm of hydrochloric acid, sulfuric acid, or nitric acid, more preferably from about 50-250 ppm hydrochloric acid, sulfuric acid, or nitric acid, and most preferably from about 100-200 ppm

hydrochloric acid, sulfuric acid, or nitric acid). Suitable organic acids include formic acid, propionic acid, p-toluenesulfonic acid, oxalic acid, and combinations thereof, and these organic acids are suitably employed within the preferred ranges of amounts as described above for the inorganic acids.

Without wishing to be bound by any particular theory, it is believed that the organic acid catalysts act as a proton source, which adds to the anhydride of dicarboxylic acid and creates a cation. The cation then quickly reacts by adding to the electronegative oxygen of the polyol. According to the present invention, addition of 5-500 ppm of the organic or inorganic acid catalyzes the selective reaction between polyol and dicarboxylic acid anhydride, and an acid group is introduced into the polyol molecule. Preferably, a triol is selected that has three hydroxyl groups per molecule. Each triol molecule is reacted with one molecule of anhydride to generate a product that has two hydroxyl groups per molecule and one ester group in the form of a carboxyl group attached to the polyol. It is preferred that the molecule produced in such addition reaction contains two hydroxyl groups, one carboxyl group and one ester group. Such chemical structure is ideal to produce low viscosity carboxyl polyols. To illustrate the relationship between chemical structure and carboxyl polyol viscosity we have plotted two graphs (refer to Figure 1 and Figure 2). Figure 1 illustrates the relationship between carboxyl polyol viscosity and the number of ester groups in the molecule of carboxyl polyol. Carboxyl polyols in Figure 1 were made by reacting 1 mole of glycerolpropoxylate ( Arch Chemicals product Poly-G 76-635 ) with 1 mole of succinic anhydride. The Carboxyl polyols in Figure 2 were obtained by reacting 1 mole of trimethylolpropane with 1 mole of succinic anhydride.

Because of the differences in starting material chemistry, trimethylolpropane- succinic anhydride reaction products are always more viscous than glycerolpropoxylate-succinic anhydride reaction products. However, if same raw materials are used carboxyl polyol has lowest viscosity if there is one ester group per molecule of resulting carboxyl polyol. Figures 1 and 2 illustrate viscosity dependence on ester group content per one carboxyl polyol molecule. Ester group content in substance was measured as the difference between the acid number at beginning of the reaction and the acid number of the carboxyl polyol. The Acid number at beginning of reaction was calculated from amounts of triol and succinic anhydride used in reaction. The Acid number of carboxyl polyol was determined by titration with sodium hydroxide solution using phenolphthalein indicator. Ester group content per one molecule was

calculated from ester group content in carboxyl polyol and molecular weight (ester content as mgKOH/g times molecular weight divided by constant 56100). Molecular weight used in calculations was number average molecular weight as determined by GPC method. Carboxyl polyol in Figure 1 containing 1.696 ester groups per molecule was obtained using method  
 5 described in U.S. Patent No. 5,863,980. Carboxyl polyol in Figure 2 containing 5.162 ester groups per molecule also was obtained using method described in U.S. Patent No. 5,863,980. These graphs demonstrate advantages of present invention in producing the desired low viscosity carboxyl polyols.

## GLYCEROL BASE CARBOXYL POLYOL VISCOSITY RELATIONSHIP AS A FUNCTION OF ESTER GROUP

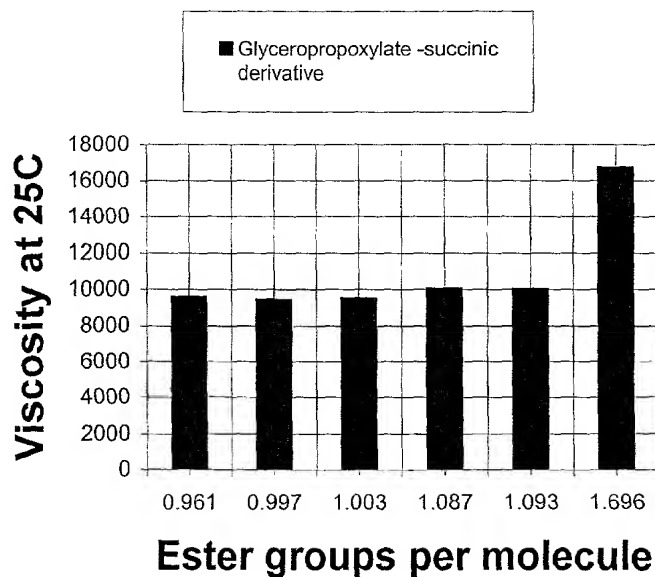
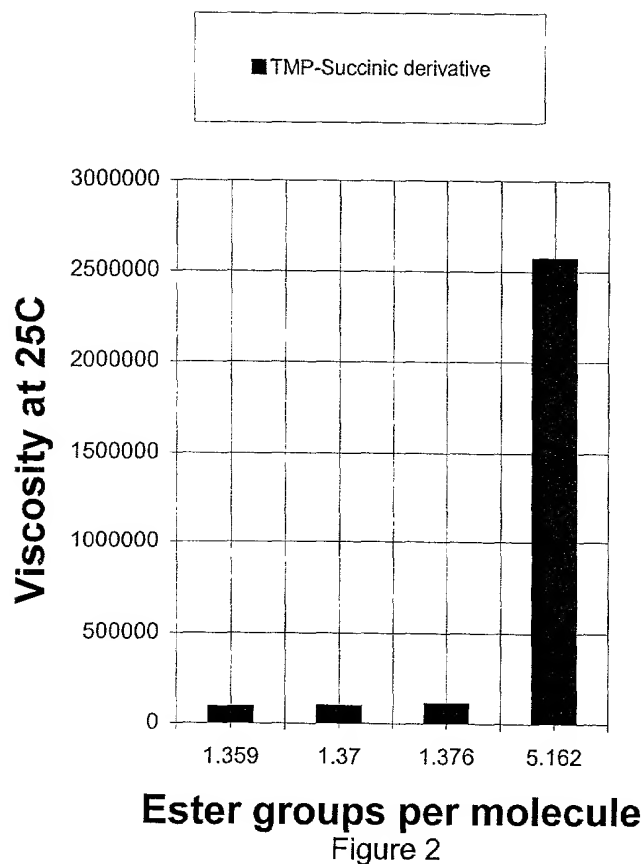


Figure 1

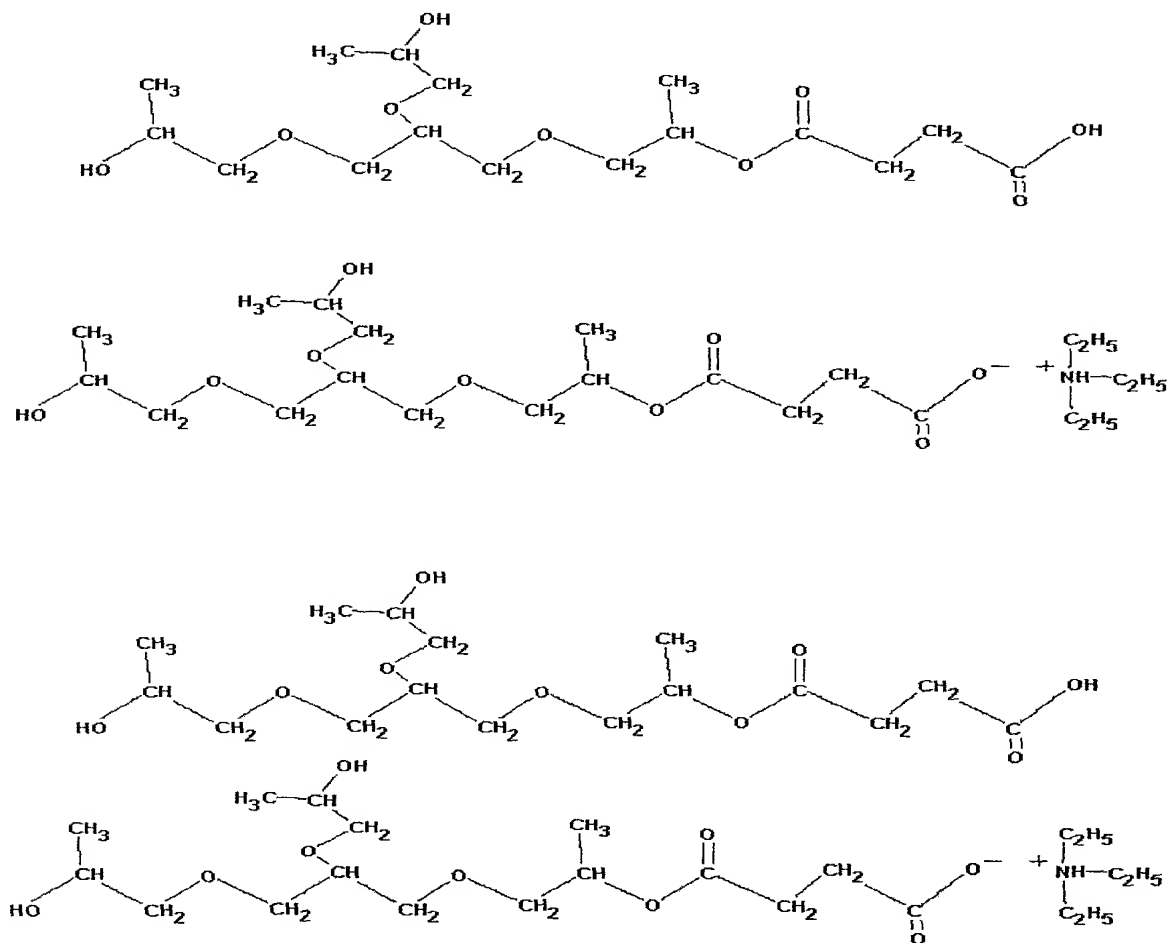


## TMP BASE CARBOXYL POLYOL VISCOSITY RELATIONSHIP AS A FUNCTION OF ESTER GROUP



To further enhance the stability of the carboxyl-containing polyols, the carboxyl group is suitably at least partially neutralized with an amine, such as triethylamine("TEA"). Besides TEA, other useful amines for neutralizing the carboxyl group on the carboxyl-containing polyol include: trimethylamine, tripropylamine, tributylamine, triisopropylamine, dimethylamine, diethylamine, dipropylamine, dibutylamine, monoethanol amine, dimethylethanolamine, aminoalcohols, morpholine, n-methylmorpholine, n- ethylmorpholine, and combinations thereof,

alone or in combinations with other organic amines. Preferably the neutralizing amine is a tertiary amine that will not react with isocyanate. Experimental polyol structures, including the TEA salt, are:



25 neutralized carboxyl polyols with isocyanate proceeds fast even at 60- 70C temperature range. All of these advantages in using neutralized carboxyl polyols amount to substantial time and energy savings.

Preferably, the carboxyl-containing monomers are liquid at room temperature because liquids are easy to handle as compared to solids. A useful range of viscosities for the carboxyl-  
30 containing monomers is generally less than 100,000 cps at 25°C. Preferably, the viscosity of the

carboxyl-containing monomers is from about 3,000 to about 100,000 cps, more preferably from about 3,000 to about 50,000 cps, and most preferably from about 3,000 to about 20,000 cps.

In order to increase the shelf life of prepolymer products made from the carboxyl-containing monomers, it is desirable that the carboxyl-containing polyols made as described above contain minimal amounts of oligomers. As defined herein, oligomers are molecules which result from the reaction of the carboxyl function with another hydroxyl function, which can lead to oligomerization of the monomer products. Oligomers are undesirable due to their propensity to cause increased viscosity of the monomer product.

It has been found that the presence of oligomers above about 30 mg KOH/g (as analyzed below) results in undesirable gelling of the prepolymer product. Preferably, the carboxyl-containing monomers have less than 30 mg KOH/g oligomers, preferably between 2 and 30 mg KOH/g oligomers, more preferably between 2 and 20 mg KOH/g oligomers, and most preferably between about 2 and 15 mg KOH/g oligomers. Oligomer content in the carboxyl-containing monomer can be measured by calculating the difference between theoretical acid number and acid number determined by chemical analysis as known in the art.

Briefly, acid number is determined using 1-2 grams of sample. 100 ml of isopropyl alcohol and 50 ml water is added to the sample, and stirred until the sample is completely dissolved. Approximately 15 drops of 1% phenolphthalein solution is added, and the sample solution is titrated with 0.5 N potassium hydroxide (or 0.5 N sodium hydroxide) until a light pink color appears. Oligomer content in the carboxyl-containing monomer can be measured by calculating the difference between theoretical acid number and acid number determined by chemical analysis (expressed as mg KOH/g sample). This difference in mg KOH/g is then correlated to oligomeric ester units per gram of monomer.

As indicated above, the carboxyl-containing polyols prepared above may be used in the production of a "prepolymer". In general, the prepolymer is made by combining the carboxyl-containing polyols prepared above with a polyisocyanate compound. Organic polyisocyanates useful as reactants in the production of the prepolymer include any aromatic, cycloaliphatic and aliphatic diisocyanates and higher polyisocyanates. Diisocyanates are the preferred class of polyisocyanates. Suitable aliphatic diisocyanates include hexamethylene diisocyanate, 4,4'-dicyclohexylmethane diisocyanate; isophorone diisocyanate; 1,4'-tetramethylene diisocyanate; and 1,10-decamethylene diisocyanate and 1,12-dodecamethylene diisocyanate. Suitable

aromatic diisocyanates include tolulene-2,4- or 2,6-diisocyanate; 1,5-naphthalene diisocyanates; 4-methoxy-1,3-phenylene diisocyanate; 4-chloro-1,3-phenylene diisocyanate; 2,4'-diisocyanatodiphenyl ether; 5,6-dimethyl-1,3-phenylate diisocyanate; 2,4-diemthyl-1,3-phenylene diisocyanate; 4,4'diisocyanatodiphenylether; benzidene diisocyanate, 4,4'-

5 diisocyanataodibenzyl; methylene-bis(4-phenylisocyanate); and 1,3-phenylene diisocyanate.

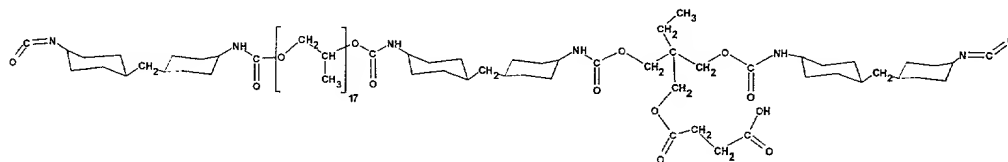
Particularly useful polyisocyanates for use in preparing the polyurethane prepolymers include toluene diisocyanate, 4,4'-diphenylmethane diisocyanate, 2,4'- diphenylmethane diisocyanate, hexamethylene diisocyanate, isophorone diisocyanate, 4,4'-dicyclohexylmethane diisocyanate, 1,12-dodecanediisocyanate, 2,4,4-trimethylhexamethylene diisocyanate, xylylene diisocyanate, 10 tetramethyl-xylylene diisocyanate and other polyisocyanates such as polymethylene polyphenyl isocyanate and isocyanate prepolymers having at least two isocyanate groups which are produced by reacting an isocyanate with a polyhydroxyl compound such as polyoxyalkylene polyol or polyester polyol or mixtures thereof.

The reaction in which hydroxyl groups are reacted with isocyanate groups and 5 polyurethane prepolymer is produced is usually performed at 50-100°C for 1-5 hours under an inert atmosphere such as nitrogen gas and at atmospheric pressure. Preferably the reaction is performed at 60-90°C for 2-3 hours.

The ratio of isocyanate to carboxyl-containing polyol is such as to have the desired amount of carboxyl groups per molecule of polyurethane prepolymer. Usually, the carboxyl- 20 containing monomer is added to result in an acid number for the prepolymer of 10-30 mg KOH/g. The preferred procedure for producing the prepolymer is to react the selected polyisocyanate with regular polyether or polyester polyol for 1-2 hours at 80-90°C, and then add carboxyl-containing monomers and react until the theoretical isocyanate group content has been reached. If desired, catalysts such as dibutyltin dilaurate, stannous octoate, or amine-type 25 catalysts like triethylamine or triethylene diamine, may be used to assist prepolymer formation. The prepolymer composition may also include solvents such as acetone, methylethylketone, N-methylpyrrolidinone, and the like.

Because of the way that carboxyl groups are added to the polyol molecule, the resulting main polyurethane chain is linear with carboxyl groups as side pendants. This structure is ideal 30 for obtaining good water-borne dispersions. The chemical structure of an exemplary prepolymer made from 1 mole of 1000 molecular weight propylene oxide based diol (Poly-G 20-112 from

Arch Chemicals, Inc., Norwalk, CT), three moles of 4,4' dicyclohexylmethane diisocyanate, and one mole of trimethylolpropane with succinic anhydride added to a side chain is as follows:



This prepolymer is easy to disperse in water by converting side pendant carboxyl groups into salt groups and then reacting free NCO groups with diamine to obtain a high molecular weight urethane dispersion in water. Because, according to the present invention, there is one carboxyl group added to each triol molecule, the resulting prepolymer has low viscosity, low oligomer content, and is very easy to disperse in water. The dispersion process proceeds easily and water-borne dispersions may be prepared without the use of high shear/high speed mixers. It has been also discovered that because prepolymers made with carboxyl polyols have low viscosity and dicarboxylic acid monoesters which are on a side chain of polyurethane molecule act as internal coalescing agents. Therefore, it is very easy to form solvent free polyurethane dispersions utilizing these prepolymers.

The prepolymer, as described above, may be combined with an amine compound to extend the prepolymer and further disperse the polymer in water. Suitable amines for dispersing prepolymer in water and chain extending the prepolymer include triethylamine, tripropylamine, ethylene diamine, n-butylamine, diethylamine, trimethylamine, monoethanol amine, dimethylethanolamine, aminoalcohols, hydrazine, hexamethylene diamine, isophorone diamine, cyclohexane diamine, dimethylcyclohexylamine, tris(3-aminopropyl)amine, 2-methylpentamethylenediamine, 1,12-dodecanediamine and combinations thereof.

The chain extension reaction occurs when free isocyanate groups of water dispersed prepolymer react with amino groups and is described in the art. The reaction between isocyanate groups and amine groups is very fast and chain extension step can be carried out in water.

It may be desirable to add other conventional additives such as thickening agents, pH adjusters, monoisocyanates and the like to the composition of the invention. Furthermore, fillers, plasticizers, pigments, and the like may be utilized as desired. It may be also desirable to add

other polyurethane prepolymers made from modified or unmodified polyether polyols or polyester polyols or the like.

## EXAMPLES

5       The following examples are intended to illustrate, but in no way limit the scope of the present invention. All parts and percentages are by weight and all temperatures are in degrees Celsius unless explicitly stated otherwise.

### Example 1 -- Connecting Carboxyl Groups to Polyether Triol

10       To a flask equipped with a thermometer, stirrer and reflux condenser were added 1696 grams of polyol Poly-G 76-635 (polyether triol with OH number 635 made by Arch Chemicals, Norwalk, CT) and 0.45 grams of 85% ortho phosphoric acid (Aldrich Chemical, St. Louis, MO). The mixture was stirred at room temperature for 30 minutes and then 645.3 grams of succinic anhydride were added (Aldrich). With agitation the working temperature was increased to 98°C and the mixture heated for 2 hours. After 2 hours, a sample for acid number was taken and compared to a theoretical value. With an acid number higher than theoretical heating was continued and then sampled every half hour until an acid number was 1 to 2 units from theoretical. When the acid number was in desired range the flask was cooled.

15       For comparison purposes, an experiment with the same polyol and succinic acid anhydride ratio except that this time no phosphoric acid was added and reaction was performed according to the procedure described in US Patent No. 5,863,980 (see Comparative Example 2 below).

20       Comparative Example 2 -- Preparing Carboxyl Polyol with no acid present in accordance with the procedure of US Patent No. 5,863,980

25       To a flask equipped with a thermometer, stirrer and reflux condenser were added 398.5 grams of polyol Poly-G 76-635 (polyether triol with OH number 635 made by Arch Chemicals, Norwalk, CT) and 152.7 grams of succinic anhydride (Aldrich). With nitrogen flow and agitation working the temperature was increased to 80°C and the mixture was heated for 1 hour. Then the

temperature was slowly raised to 135C over time span of about 30 minutes, and reaction performed at the same temperature for two hours. Product was heated at 135C and vacuum stripped at -29 inches of mercury for 2 hours. Flask was cooled under vacuum.

5 The resulting polyols are compared in Table 1.

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**Table 1****Comparison of acid catalysis effect on carboxyl polyol synthesis**

Formulation of:	Comp. Example 2 (Prior Art)	Example 1 (Present Invention)
Triol Used	Polyether Polyol 76-635 from Arch Chemical	Polyether Polyol 76-635 from Arch Chemical
H <sub>3</sub> PO <sub>4</sub> , ppm	0	227
Temp. (°C)	135	98
Theoretical Acid	155.2	155.2
Found Acid	120	153
Oligoester, mg KOH/g	35.2	2.2
Oligoester/Acid	0.2933	0.014
OH #	289	321
PH	3.4	3.3
Viscosity at 25C	16720	8800
MW by GPC	500	408
Calculated MW	361	361
MW Difference	139	47

5 The data in Table 1 show that the polyol obtained according to the prior art was 1.9 times more viscous and contained 16 times more oligoester units. Also there was significant difference between the molecular weight determined by GPC for this polyol and that calculated from the formula. Polyol with carboxyl groups made according to this invention was less viscous, contained only few oligoester groups and the molecular weight determined by GPC was close to the theoretical molecular weight calculated.

10 Polyols obtained in experiments 1 and 2 above were reacted with 2000 molecular weight polyether diol Poly-G 20-56 (made by Arch Chemicals) and 4,4'-dicyclohexylmethane diisocyanate (Desmodur W made by Bayer) to produce prepolymers (refer to the formulations described in Comparative Example 3 and Example 4 in Table 2 below). Table 2 compares properties of the prepolymer obtained in the process of this invention (Example 4) with that  
15 obtained according to the process of US Patent 5,863,980 ("Prior Art") (Comparative Example 3).



**Table 2****Prepolymer Comparison of Prior Art to Present Invention**

	<b>Experiment 3 (Prior Art)</b>	<b>Experiment 4 (Present Invention)</b>
Raw Materials Used	Polyol of Comp. Exp. 2, Polyether diol, Poly-G 20-56, Desmodur W	Polyol of Exp. 1, Polyether diol, Poly-G 20-56, Desmodur W
NCO/OH ratio	1.3	1.3
Acid # of Prepolymer	30.8	31.3
NCO% Theoretical	2.06	2.00
NCO% After Reaction	2.19	2.14
Viscosity at 25C (measured after reaction)	416,000	11,160
NCO% After 16 Hours	gel	2.13
Viscosity at 25C After 16 Hours	gel	21,520

As can be seen in Table 2, prepolymer obtained from polyol made according to US Patent 5,863,980 was 37 times more viscous than prepolymer made with carboxyl containing polyol made through the current invention and eventually gelled after 15 hours. Table 3 contains data on the results of connecting carboxyl groups to different triols by the addition reaction of the present invention.

In Table 3, formulations and properties are provided for compositions prepared in accordance with Example 1 above, and these compositions are identified in Table 3 as Examples 1, 5, 6, 7, and 12. The preparation for Example 8 is described below, and Examples 9, 10 and 11 were prepared in accordance with the protocol given in Example 8.

**Table 3.** Effect of connecting carboxyl groups to triols

Example No.	1 (above)	5	6	7	8	9	10	11	12
Triol Used	Polyether Polyol 76-635	Polyether Polyol 76-635	Polyether Polyol 76-635	Polyether Polyol 76-635	TMP	TMP	TMP	TMP	Polyether Polyol 35-610 from Arch Chemicals
Phosphoric Acid ppm	227	5	5	227	316	316	300	320	5
Temp. C	98	100	100	98	100	100	80	103	80
Theoretical Acid #	155.2	155.2	155.2	155.2	239.5	239.5	239.5	239.5	150.9
Found Acid #	153	150.7	146.7	149.3	224.5	219	227.5	213.4	147.8
Oligoester, mgKOH/g	2.2	4.5	8.5	5.9	15	20.5	12	26.1	3.1
Oligoester/Acid	0.014	0.030	0.058	0.0395	0.067	0.086	0.0527	0.1223	0.0209
OH #	321	322	311	316	449.7	451	455.3	439.7	300.7
Water %	0.2	0.3	0.05	.05	0.6	0.31	0.41	0.41	0.24
pH	3.3	3.1	3.1	3.3	3.2	3.1	3.1	3.1	3.2
Viscosity at 25C	8800	11500	12600	8840	97200	108400	77600	90800	4265
MW by GPC	408	392	405	408	302	297	315	287	374
Calculated MW	361	361	361	361	234	234	234	234	371.9
MW Difference	47	31	44	47	68	63	81	53	2.1

In Table 3, "TMP" denotes trimethylolpropane.

Example 8 – Addition Reaction Connecting Carboxyl Groups to Trimethylolpropane

To a flask equipped with thermometer, stirrer and reflux condenser were added 1341.8 grams of trimethylolpropane (Aldrich). Without agitation the temperature was slowly increased to 95°C to melt the trimethylolpropane. To the melted trimethylolpropane melted were added 0.753 grams of 85% ortho phosphoric acid (Aldrich) and 1000.7 grams of succinic anhydride (Aldrich). With agitation, the slurry was heated to and held at 100°C until all solids were dissolved. As soon as there were no solids in the flask, it was sampled for acid number and compared to the theoretical value. With acid number higher than theoretical, heat was continued and sampled every 15 minutes till an acid number was 1 to 2 units from theoretical. When the acid number was in desired range the flask was cooled.

Example 13 -- Preparation of Water-Borne Polyurethane Dispersion.

38 grams of 4,4'-dicyclohexylmethane diisocyanate ("DESMODUR W" from by Bayer), 22.3 of polyether diol with molecular weight 425 (Poly-G 20-265 from Arch Chemicals), 0.008 grams of dibutyltin dilaurate (catalyst Dabco T-12 from Air Products), and 18.7 grams of methylethylketone were mixed and heated to 85°C and maintained at that temperature for 1 hour. After 1 hour, 21 grams of carboxyl polyol was added. This carboxyl polyol was obtained by reacting 1 mol of Poly-G 76-635 with 1 mol of succinic anhydride as described in Example 1, and had an equivalent weight of 179.4 for each OH group, and an equivalent weight 381.6 for each carboxyl group. After adding the carboxyl polyol, heating was continued for 2 more hours at 85°C. The NCO content of the prepolymer was analyzed and found to be 3.08%. The warm prepolymer was mixed at a high speed and then a mixture of 5.56 grams of triethylamine and 100 grams of water were added and mixed for 5 minutes to insure complete dispersion. No heating was applied at this stage. Temperature in flask after adding triethylamine and water was 46-47°C. A solution of 2.09 grams of ethylenediamine in 56.7 grams water was added to the dispersion and agitation was continued for 1 hour. The resulting dispersion was an opalescent liquid which after drying produced film with the following physical properties: Sward Hardness: 49; Tensile Strength: 3720 psi; Elongation at break: 52%

Example 14 -- Preparation of Water-Borne Polyurethane Dispersion

62.07 grams of 4,4'-dicyclohexylmethane diisocyanate ("DESMODUR W" from Bayer), 70 grams of polyether diol with molecular weight 1000 (Poly-G 20-112 from Arch Chemicals), 0.062 grams of dibutyltin dilaurate (Dabco T-12 from Air Products), 39.25 grams of methylethylketone was mixed and heated to 85°C and maintained at that temperature for 1 hour. After 1 hour, 28.87 grams of carboxyl polyol was added. This carboxyl polyol was obtained by reacting 1 mol of trimethylolpropane with 1 mol of succinic anhydride as described in Example 8 and had equivalent weight 127.9 for each OH group and equivalent weight 268.4 for each carboxyl group. After adding carboxyl polyol heating was continued for 2 more hours at 85°C. The NCO content of prepolymer was analyzed and found to be 2.34%. Warm prepolymer was mixed fast and mixture of 10.82 grams of triethylamine and 200 grams of water was added and mixed for 5 minutes to insure complete dispersion. No heating to flask was applied at this stage. Temperature in flask after adding of triethylamine and water was 49-50°C. Solution of 3.16 grams of ethylenediamine in 163.4 grams of water was added to dispersion and agitation was continued for 2 hours. The resulting dispersion was opalescent liquid which after drying produced film with following physical properties: Sward Hardness: 29; Tensile Strength: 3960 psi; Elongation at break: 265%; 100% modulus: 2220 psi; Tear resistance: 265 p/in.

Example 15 - Preparing Carboxyl Polyol in Presence of Hydrochloric Acid

To a flask equipped with a thermometer, stirrer and reflux condenser were added 494.8 grams of polyol Poly-G 76-635 (polyether triol with OH number 635 made by Arch Chemicals, Norwalk, CT) and 0.132 grams of 35% hydrochloric acid (Aldrich Chemical, St. Louis, MO). The mixture was stirred at room temperature for 10 minutes and then 188.26 grams of succinic anhydride were added (Aldrich). With agitation the working temperature was increased to 100°C and the mixture was heated for 2 hours. After 2 hours, a sample for acid number was taken and compared to a theoretical value. With an acid number higher than theoretical heating was continued and then sampled every half hour till an acid number was 1 to 2 units from theoretical. When the acid number was in the desired range the flask was cooled.

Example 16 – Preparing Carboxyl Polyol in Presence of Sulfuric Acid

To a flask equipped with a thermometer, stirrer and reflux condenser were added 494.8 grams of polyol Poly-G 76-635 (polyether triol with OH number 635 made by Arch Chemicals, Norwalk, CT) and 0.060 grams of 100% sulfuric acid (Aldrich Chemical, St. Louis, MO). The mixture was stirred at room temperature for 10 minutes and then 188.26 grams of succinic anhydride were added (Aldrich). With agitation the working temperature was increased to 100°C and the mixture was heated for 2 hours. After 2 hours, a sample for acid number was taken and compared to a theoretical value. With an acid number higher than theoretical heating was continued and then sampled every half hour till an acid number was 1 to 2 units from theoretical. When the acid number was in the desired range the the flask was cooled.

Example 17 -- Preparing Carboxyl Polyol in Presence of Nitric Acid

To a flask equipped with a thermometer, stirrer and reflux condenser were added 398.5 grams of polyol Poly-G 76-635 (polyether triol with OH number 635 made by Arch Chemicals, Norwalk, CT), 0.072 grams of 70% nitric acid (Aldrich Chemical, St. Louis, MO) and 152.6 grams of succinic anhydride were added (Aldrich). With agitation the working temperature was increased to 100°C and the mixture was heated for 2 hours. After 2.5 hours, a sample for acid number was taken and compared to a theoretical value. With an acid number higher than theoretical heating was continued and then sampled every half hour till an acid number was 1 to 2 units from theoretical. When the acid number was in the desired range the flask was cooled.

Table 4 shows comparative results in the production of carboxyl polyols using phosphoric acid (Examples 1 and 5 above), hydrochloric acid (Example 15), sulfuric acid (Example 16), and nitric acid (Example 17) as catalysts.

**Table 4.** Properties of Carboxyl Polyols made in presence of inorganic acid catalysts

Exp. No.	1	5	15	16	17
Triol Used	Polyether Polyol 76-635	Polyether Polyol 76-635	Polyether Polyol 76-635	Polyether Polyol 76-635	Polyether Polyol 76-635
Acid used	Phosphoric	Phosphoric	Hydrochloric	Sulfuric	Nitric
Acid ppm	227	5	193	88	130
Temp. °C	98	98	100	100	100
Theoretical Acid #	155.2	155.2	155.2	155.2	155.2
Found Acid #	153	150.7	154.4	153.8	154.4
Oligomer mgKOH/g	2.2	4.5	0.8	1.4	0.8
Oligomer/Acid	0.014	0.030	0.005	0.009	0.005
OH #	321	322	332	334	327
Water %	0.2	0.3	0.08	0.08	0.08
pH	3.3	3.1	3.3	3.2	3.4
Viscosity at 25C	8800	11500	7680	7280	9100
MW by GPC	408	392	455	460	453
Calculated MW	361	361	361	361	361
MW Difference	47	31	94	99	92

Example 18-- Preparation of Water-Borne Polyurethane Dispersion

52.85 grams of isophorone diisocyanate ("LUXATE IM" from Lyondell Chemical Co., Houston, TX), 69.4 grams of polyether diol with molecular weight 1000 (Poly-G 20-112 made by Arch Chemicals, Norwalk, CT), 0.08 grams of dibutyltin dilaurate (Dabco T-12 from Air Products, Allentown, PA), 39.25 grams of methylethylketone was mixed and heated to 85°C and maintained at that temperature for 1 hour. After 1 hour 38.5 grams of polyol with carboxyl groups was added. This carboxyl polyol was obtained by reacting 1 mol of polyether polyol 76-635 with 1 mol of succinic anhydride in presence of hydrochloric acid as described in Example 15 and had equivalent weight 168.8 for each OH group and equivalent weight 358.7 for each carboxyl group. After adding polyol with carboxyl groups heating was continued for 3 more hours at 85°C. The NCO content of prepolymer was analyzed and found to be 2.16%. Warm prepolymer was mixed fast and mixture of 10.9 grams of triethylamine and 300 grams of water was added and mixed for 5 minutes to insure complete dispersion. No heating to flask was applied at this stage. Temperature in flask after adding of triethylamine and water was 49-50°C. Solution of 8.29 grams of isophorone diamine in 200 grams of water was added to dispersion and agitation was continued for 2 hours. The resulting dispersion was opalescent liquid which after drying produced film with following physical properties: Sward Hardness: 24; Tensile Strength: 3780 psi; Elongation at break: 488%; 100% modulus: 910 psi; Tear resistance: 244 p/in.

Example 19 -- Preparation of Water-Borne Polyurethane Dispersion

52.9 grams of isophorone diisocyanate ("LUXATE IM" from Lyondell Chemical Co., Houston, TX), 69.4 grams of polyether diol with molecular weight 1000 (Poly-G 20-112 made by Arch Chemicals, Norwalk, CT), 0.1 grams of dibutyltin dilaurate (Dabco T-12 from Air Products, Allentown, PA), 39.25 grams of methylethylketone was mixed and heated to 85°C and maintained at that temperature for 1 hour. After 1 hour 38.4 grams of polyol with carboxyl groups was added. This polyol with carboxyl groups was obtained by reacting 1 mol of polyether polyol 76-635 with 1 mol of succinic anhydride in presence of sulfuric acid as described in Example 16 and had equivalent weight 167.8 for each OH group and equivalent weight 353.7 for each carboxyl group. After adding polyol with carboxyl groups, heating was continued for 3 more hours at 85°C. The NCO content of prepolymer was analyzed and found to be 2.26%. Warm prepolymer was mixed fast and mixture of 11 grams of triethylamine and 300

grams of water was added and mixed for 5 minutes to insure complete dispersion. No heating to flask was applied at this stage. Temperature in flask after adding of triethylamine and water was 49-50°C. Solution of 8.2 grams of isophorone diamine in 200 grams of water was added to dispersion and agitation was continued for 2 hours. The resulting dispersion was opalescent liquid which after drying produced film with following physical properties: Sward Hardness: 24; Tensile Strength: 3310 psi; Elongation at break: 470%; 100% modulus: 910 psi; Tear resistance: 270 p/in.

#### Example 20 -- Preparation of Water-Borne Polyurethane Dispersion

158.6 grams of isophorone diisocyanate ("LUXATE IM" from Lyondell Chemical Co., Houston, TX), 206.9 grams of polyether diol with molecular weight 1000 (Poly-G 20-112 made by Arch Chemicals, Norwalk, CT), 0.6 grams of dibutyltin dilaurate (Dabco T-12 from Air Products, Allentown, PA), 117.8 grams of N-methylpyrrolidinone was mixed and heated to 85°C and maintained at that temperature for 3 hours. After 3 hours 116.8 grams of polyol with carboxyl groups was added. This polyol with carboxyl groups was obtained by reacting 1 mol of polyether polyol 76-635 with 1 mol of succinic anhydride in presence of nitric acid as described in Example 17 and had equivalent weight 167.8 for each OH group and equivalent weight 363.3 for each carboxyl group. After adding polyol with carboxyl groups heating was continued for 3 more hours at 85°C. The NCO content of prepolymer was analyzed and found to be 2.55%. Viscosity at 25 °C was 42560 cP. This prepolymer was cooled to room temperature and used for preparation of water borne polyurethane dispersions as described in the following Examples.

#### Example 21 -- Preparation Of Water Borne Polyurethane Dispersion

Prepolymer was made as described in Example 20. 300 grams of water at room temperature were placed in 1-liter flask equipped with mechanical stirrer, 0.1 grams of surfactant BYK 020 (BYK Chemie) and 5.4 grams of triethylamine (Aldrich) were added to water. The contents of the flask was stirred and 91.1 grams of prepolymer was slowly added to the flask. After all prepolymer has been dispersed in water, 2.87 grams of cyclohexyl diamine was dissolved in 30 grams of water and drop wise added to dispersed prepolymer. The flask was stirred without heating for 4 hours. The resulting dispersion was an opalescent liquid which after



drying produced film with following physical properties: Sward Hardness 24, Tensile Strength 2603 psi, Elongation at break 830%, 100% modulus 381 psi, Tear resistance 88 p/in.

Example 22 -- Preparation Of Water Borne Polyurethane Dispersion

5       Prepolymer was made as described in Example 20. 300 grams of water at room temperature was placed in 1-liter flask equipped with mechanical stirrer, 0.1 grams of surfactant BYK 020 (BYK Chemie) and 5.4 grams of triethylamine (Aldrich) were added to the water. Contents of the flask was stirred, and 103.4 grams of prepolymer was slowly added to the flask. After all the prepolymer has been dispersed in water 1.71 grams of ethylenediamine was  
10       dissolved in 30 grams of water and drop wise added to disperse prepolymer. The flask was stirred without heating 4 hours. The resulting dispersion was an opalescent liquid which after drying produced film with following physical properties: Sward Hardness 22, Tensile Strength 1280 psi, Elongation at break 685%, 100% modulus 240 psi, Tear resistance 77 p/in.

15       Example 23 - Preparation Of Water Borne Polyurethane Dispersion

Prepolymer was made as described in Example 20. 300 grams of water at room temperature were placed in 1-liter flask equipped with mechanical stirrer, 0.1 grams of surfactant BYK 020 (BYK Chemie) and 5.4 grams of triethylamine (Aldrich) were added to the water. The contents of the flask were stirred, and 99.7 grams of prepolymer was slowly added to the  
20       flask. After all prepolymer has been dispersed in water, 4.7 grams of isophorone diamine was dissolved in 30 grams of water and drop wise added to the dispersed prepolymer. The flask was stirred without heating 4 hours. The resulting dispersion was an opalescent liquid which after drying produced a film with following physical properties: Sward Hardness 24, Tensile Strength 1745 psi, Elongation at break 526%, 100% modulus 291 psi, Tear resistance 87 p/in.

25       Example 24 - Preparation Of Water Borne Polyurethane Dispersion

Prepolymer was made as described in Example 20. 300 grams of water at room temperature were placed in a 1-liter flask equipped with mechanical stirrer, and 0.1 grams of surfactant BYK 020 (BYK Chemie) and 5.4 grams of triethylamine (Aldrich) were added to the  
30       water. The contents of flask were stirred, and 114.5 grams of prepolymer was slowly added to the flask. After all prepolymer had been dispersed in water, 2.88 grams of 35% hydrazine was

dissolved in 30 grams of water and drop wise added to the dispersed prepolymer. The flask was stirred without heating 4 hours. The resulting dispersion was an opalescent liquid which after drying produced a film with following physical properties: Sward Hardness 20, Tensile Strength 1020 psi, Elongation at break 860%, 100% modulus 218 psi, Tear resistance 73 p/in.

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#### Example 25 – Preparing Carboxyl Polyol in Presence of Formic Acid

To a flask equipped with a thermometer, stirrer and reflux condenser were added 398.5 grams of polyol Poly-G 76-635 (polyether triol with OH number 635 made by Arch Chemicals, Norwalk, CT) and 0.126 grams of 96% formic acid (Aldrich Chemical, St. Louis, MO). The mixture was stirred at room temperature for 10 minutes and then 151.7 grams of succinic anhydride were added (Aldrich). With agitation the working temperature was increased to 100°C and the mixture was heated for 4 hours. After 4 hours, a sample for acid number was taken and compared to a theoretical value. With an acid number higher than theoretical heating was continued and then sampled every half hour till an acid number was 1 to 2 units from theoretical. When the acid number was in the desired range the flask was cooled.

#### Example 26 – Preparing Carboxyl Polyol in Presence of Propionic Acid

To a flask equipped with a thermometer, stirrer and reflux condenser were added 398.5 grams of polyol Poly-G 76-635 (polyether triol with OH number 635 made by Arch Chemicals, Norwalk, CT), 0.126 grams of 99% propionic acid (Aldrich Chemical, St. Louis, MO) and 151.7 grams of succinic anhydride were added (Aldrich). With agitation the working temperature was increased to 100°C and the mixture was heated for 4 hours. After 4 hours, a sample for acid number was taken and compared to a theoretical value. With an acid number higher than theoretical heating was continued and then sampled every half hour till an acid number was 1 to 2 units from theoretical. When the acid number was in the desired range the flask was cooled.

#### Example 27 – Preparing Carboxyl Polyol in Presence of p-Toluenesulfonic acid

To a flask equipped with a thermometer, stirrer and reflux condenser were added 398.5 grams of polyol Poly-G 76-635 (polyether triol with OH number 635 made by Arch Chemicals, Norwalk, CT) and 0.124 grams of 98% p-toluenesulfonic acid (Aldrich Chemical, St. Louis, MO). The mixture was stirred at room temperature for 10 minutes and then 151.7 grams of succinic

anhydride were added (Aldrich). With agitation the working temperature was increased to 100°C and the mixture was heated for 4 hours. After 4 hours, a sample for acid number was taken and compared to a theoretical value. With an acid number higher than theoretical heating was continued and then sampled every half hour till an acid number was 1 to 2 units from theoretical. When the acid number was in the desired range the flask was cooled.

Example 28 – Preparing Carboxyl Polyol in Presence of Oxalic Acid

To a flask equipped with a thermometer, stirrer and reflux condenser were added 398.5 grams of polyol Poly-G 76-635 (polyether triol with OH number 635 made by Arch Chemicals, Norwalk, CT) and 0.127 grams of 98% oxalic acid (Aldrich Chemical, St. Louis, MO). The mixture was stirred at room temperature for 10 minutes and then 151.7 grams of succinic anhydride were added (Aldrich). With agitation the working temperature was increased to 100°C and the mixture was heated for 4 hours. After 4 hours, a sample for acid number was taken and compared to a theoretical value. With an acid number higher than theoretical heating was continued and then sampled every half hour till an acid number was 1 to 2 units from theoretical. When the acid number was in the desired range the flask was cooled.

As it is seen from the results given in Table 5, the illustrative organic acids can be used to produce carboxyl polyols with oligomer content less than 2 mgKOH/g. These polyols with carboxyl groups are particularly useful in waterborne polyurethane dispersions.

**Table 5. Properties of Carboxyl Polyols made in presence of organic acid catalysts**

Exp. No.	25	26	28	27
Triol Used	Polyether Polyol 76-635	Polyether Polyol 76-635	Polyether Polyol 76-635	Polyether Polyol 76-635
Acid used	Formic	Propionic	Oxalic	p-toluene sulfonic
Acid ppm	230	230	230	230
Temp. C	100	100	100	100
Theoretical Acid #	155.2	155.2	155.2	155.2
Found Acid #	154.5	154.5	153.2	153.6
Oligomer mgKOH/g	0.7	0.8	1.0	1.6
Oligomer/Acid	0.005	0.005	0.006	0.01
OH #	315	313	312.5	312
Water %	0.19	0.15	0.19	0.26
PH	3.3	3.3	3.3	3.3
Viscosity at 25C	9600	9500	10020	10040
Mol weight by GPC	346	361	390	389
Calculated mol weight	361	361	361	361
Mol weight difference	15	0	29	28

**Example 29** Preparing of 100% neutralized Carboxyl Polyol

To a flask equipped with a thermometer, stirrer, reflux condenser and nitrogen inlet were added 506.9 grams of polyol Poly-G 76-635 (polyether triol with OH number 635 made by Arch Chemicals, Norwalk, CT) and 0.14 grams of 95% phosphoric acid (Aldrich Chemical, St.

Louis, MO). The mixture was stirred at room temperature for 10 minutes and then 192.9 grams of succinic anhydride were added (Aldrich). With agitation the working temperature was increased to 100°C and the mixture was heated for 4 hours. After 4 hours, a sample for acid number was taken. Heating was continued and then sampled every half hour till an acid number was 150 to 152 units. When the acid number was in the desired range the flask was cooled to 80C. With good mixing and using an addition funnel 202 grams of triethylamine was added in

such rate as not to exceed 85C temperature in flask. After all triethylamine was added the mixing and cooling was continued till temperature in flask was 50C or less.

Example 30 - Preparing polyurethane dispersion using 100% neutralized Carboxyl Polyol

5 52.5 grams of isophorone diisocyanate ("LUXATE IM" from Lyondell Chemical Co., Houston, TX), 115.6 grams of polyether diol with molecular weight 2000 (Poly-G 20-56 made by Arch Chemicals, Norwalk, CT), 0.01 grams of dibutyltin dilaurate (Dabco T-12 from Air Products, Allentown, PA), 50 grams of methyl ethyl ketone was mixed and heated to 80°C and maintained at that temperature for 3 hours. After 3 hours 31.8 grams of 100% neutralized  
10 carboxyl polyol obtained as in example 51 was added. This polyol with carboxyl had equivalent weight 219 for each OH group and equivalent weight 474 for each carboxyl group. After adding polyol with carboxyl groups heating was continued for 1.5 more hours at 80°C. The NCO content of prepolymer was analyzed and found to be 3.67%. This prepolymer was cooled to 65C temperature and 250 grams of room temperature water was added in 2-3 minutes with good  
15 mixing. Prepolymer dispersion in water was later reacted with solution of 5.99 ethylene diamine in 131.5 grams of water. This ethylene diamine-water solution was slowly added thru addition funnel during 8-10 minutes with good agitation. Mixing was continued till no isocyanate groups could be found by IR method. The resulting dispersion was an opalescent liquid which after drying produced a film with following physical properties: Sward Hardness 20, Tensile Strength  
20 4180 psi, Elongation at break 790%, 100% modulus 660 psi, Tear resistance 240 p/in.

Example 31 - Preparing of 50 % neutralized Carboxyl Polyol

To a flask equipped with a thermometer, stirrer, reflux condenser and nitrogen inlet were added 506.9 grams of polyol Poly-G 76-635 (polyether triol with OH number 635 made by Arch  
25 Chemicals, Norwalk, CT) and 0.14 grams of 95% phosphoric acid (Aldrich Chemical, St. Louis, MO). The mixture was stirred at room temperature for 10 minutes and then 192.9 grams of succinic anhydride were added (Aldrich). With agitation the working temperature was increased to 100°C and the mixture was heated for 4 hours. After 4 hours, a sample for acid number was taken. Heating was continued and then sampled every half hour till an acid number  
30 was 150 to 152 units. When the acid number was in the desired range the flask was cooled to 80C. With good mixing and using an addition funnel 101 grams of triethylamine was added in

such rate as not to exceed 85C temperature in flask. After all triethylamine was added the mixing and cooling was continued till temperature in flask was 50C or less.

Example 32 - Preparing polyurethane dispersion using 50 % neutralized Carboxyl Polyol

200 grams of 4,4'-dicyclohexylmethane diisocyanate ("DESMODUR W" from Bayer), 257 grams of polyether diol with molecular weight 2000 (Poly-G 20-56 made by Arch Chemicals, Norwalk, CT), 0.2 grams of dibutyltin dilaurate (Dabco T-12 from Air Products, Allentown, PA), 137 grams of N-methylpyrrolidinone was mixed and heated to 85°C and maintained at that temperature for 2 hours. After 2 hours 105.9 grams of 50% neutralized carboxyl polyol obtained as in example 53 was added. This carboxyl polyol had equivalent weight 209.5 for each OH group and equivalent weight 424 for each carboxyl group. Reaction mixture was cooled to 60C. After adding polyol with carboxyl groups heating was continued for 5 more hours at 60°C. Prepolymer was cooled to room temperature and kept under nitrogen blanket over night. The NCO content of prepolymer was analyzed and found to be 4.86 %. Viscosity at 25C temperature was 2520 cp. 210 grams of this prepolymer were added to 240 grams of room temperature water with good mixing. Prepolymer dispersion in water was later reacted with solution of 6.93 g ethylene diamine in 53 grams of water. This ethylene diamine-water solution was slowly added thru addition funnel during 8-10 minutes with good agitation. Mixing was continued till no isocyanate groups could be found by IR method. The resulting dispersion was an opalescent liquid which after drying produced a film with following physical properties: Sward Hardness 32, Tensile Strength 5500 psi, Elongation at break 470%, 100% modulus 2100 psi, Tear resistance 435 p/in.

Example 33 - Preparing polyurethane dispersion using 50 % neutralized Carboxyl Polyol

391.6 grams isophorone diisocyanate ("LUXATE IM" from Lyondell Chemical Co., Houston, TX), 418.2 grams of polyether diol with molecular weight 100 (Poly-G 20-112 made by Arch Chemicals, Norwalk, CT), 0.029 grams of dibutyltin dilaurate (Dabco T-12 from Air Products, Allentown, PA), 274 grams of N-methylpyrrolidinone was mixed and heated to 85°C and maintained at that temperature for 2 hours. After 2 hours 316 grams of 50% neutralized carboxyl polyol obtained as in example 53 was added. This carboxyl polyol had equivalent weight 209.5 for each OH group and equivalent weight 424 for each carboxyl group. Reaction

mixture was cooled to 60C. After adding polyol with carboxyl groups heating was continued for 2 more hours at 60°C. Prepolymer was cooled to room temperature and kept under nitrogen blanket over night. The NCO content of prepolymer was analyzed and found to be 3.65 %.

Viscosity at 25C temperature was 5680 cp. 315 grams of this prepolymer were added to 360 grams of room temperature with good mixing. Prepolymer dispersion in water was later reacted with solution of 16.64 g isophorone diamine in 80 grams of water. This isophorone diamine-water solution was slowly added thru addition funnel during 8-10 minutes with good agitation. Mixing was continued till no isocyanate groups could be found by IR method. The resulting dispersion was an opalescent liquid which after drying produced a film with following physical properties: Sward Hardness 26, Tensile Strength 5550 psi, Elongation at break 315%, 100% modulus 2150 psi, Tear resistance 270 p/in.

Example 34 - Preparing solvent free polyurethane dispersion using 50 % neutralized Carboxyl Polyol

124.7 grams isophorone diisocyanate ("LUXATE IM" from Lyondell Chemical Co., Houston, TX), 164.45 grams of polyether diol with molecular weight 100 (Poly-G 20-112 made by Arch Chemicals, Norwalk, CT), 0.014 grams of dibutyltin dilaurate (Dabco T-12 from Air Products, Allentown, PA) was mixed and heated to 85°C and maintained at that temperature for 2 hours. After 2 hours 85.5 grams of 50% neutralized carboxyl polyol obtained as in example 53 was added. This carboxyl polyol had equivalent weight 209.5 for each OH group and equivalent weight 424 for each carboxyl group. Reaction mixture was cooled to 60C. After adding polyol with carboxyl groups heating was continued for 2 more hours at 60°C. After that reaction time temperature in flask was gradually raised to 70C during 10-15 minutes period. Prepolymer was analyzed and found to have NCO%= 4.6. Viscosity of prepolymer at 70C was 6800 cp. 261 grams of this prepolymer at 70C temperature were added to 401 grams of temperature at 40C temperature with good mixing. Prepolymer dispersion in water was later reacted with solution of 11.39 g isophorone diamine in 90 grams of water. This isophorone diamine-water solution was slowly added thru addition funnel during 8-10 minutes with good agitation. Mixing was continued till no isocyanate groups could be found by IR method. The resulting dispersion was an opalescent liquid which after drying produced a film with following

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